

Time evolution of NaCl flux through the microbial cellulose membrane with concentration polarization

SŁAWOMIR GRZEGORCZYN¹, KATARZYNA MICHALSKA-MAŁECKA²,
ANDRZEJ ŚLĘZAK³

¹Department of Biophysics, Silesia Medical University, Zabrze

²Department of Ophthalmology, Silesia Medical University, Sosnowiec

³Chair of Biomedical Fundamentals of Sport, Częstochowa University of Technology,
Częstochowa

Summary

The method of solute permeability coefficient and solute fluxes appointment for the membrane, based on monitoring of changes of conductivity of electrolyte solutions was presented. It was stated that during mechanical stirring of solutions the coefficient of NaCl permeability for microbial cellulose membrane (*Biofill*) did not depend on configuration of the membrane system and concentrations of solutions. Time characteristics of NaCl flux through the membrane *Biofill* oriented in horizontal plane were measured and modeled.

The changes of NaCl fluxes through the membrane *Biofill* caused by concentration boundary layers build up on both sides of the membrane depended on NaCl concentrations and configuration of the membrane system. The differences between fluxes in different configurations of the membrane system were observed after time depended on initial concentrations in chambers. After that time, for configuration with solution with higher density over the membrane (configuration B) the NaCl flux through the membrane was greater than for configuration with solution with lower density over the membrane (configuration A).

Besides it was stated that the coefficient of concentration polarization for configuration B was higher than for configuration A for all studied NaCl concentrations. Increase of mean concentration in the membrane at the initial moment caused increase (for configuration B) and lack of changes (for configuration A) of concentration polarization coefficient in the steady state of the membrane system.

The interpretation of experimental results was made on the basis of Kedem-Katchalsky equations for the membrane system.

Key words: microbial cellulose membrane, Kedem-Katchalsky equations, concentration polarization coefficient

Czasowa ewolucja strumienia NaCl przez membranę z celulozy bakteryjnej z polaryzacją stężeniową

Streszczenie

Przedstawiono metodę wyznaczania współczynnika przepuszczalności i strumienia substancji rozpuszczonej membrany, opartą na monitorowaniu zmian przewodnictwa roztworów elektrolitu. Ustalono, że podczas mechanicznego mieszania roztworów, współczynnik przepuszczalności NaCl dla membrany z celulozy bakteryjnej (*Biofill*) nie zależy od konfiguracji układu membranowego i stężeń roztworów. Zmierzono i obliczono czasowe charakterystyki strumienia NaCl przez membranę *Biofill* zorientowaną w płaszczyźnie horyzontalnej.

Zmiany strumieni NaCl przez membranę *Biofill*, były spowodowane przez stężeniowe warstwy graniczne utworzone po obydwu stronach membrany, zależne od stężenia NaCl i konfiguracji układu membranowego. Różnice między strumieniami w różnych konfiguracjach układu membranowego, zaobserwowano po czasie zależnym od stężenia początkowego roztworu. Po tym czasie, dla konfiguracji z roztworem o większej gęstości nad membraną (konfiguracja B) strumień NaCl przez membranę jest większy, niż dla konfiguracji z roztworem o mniejszej gęstości nad membraną (konfiguracja A).

Ponadto wykazano, że wartości współczynnika polaryzacji stężeniowej dla konfiguracji B są większe niż dla konfiguracji A. Zwiększenie średniego stężenia w membranie w chwili początkowej, spowodowało zwiększenie (dla konfiguracji B) i brak zmian (dla konfiguracji A) współczynnika polaryzacji stężeniowej, w stanie ustalonym układu membranowego. Interpretację wyników badań doświadczalnych przeprowadzono w oparciu o równania Kedem-Katchalsky'ego.

Słowa kluczowe: membrana z celulozy bakteryjnej, równania Kedem-Katchalsky'ego, współczynnik polaryzacji stężeniowej

INTRODUCTION

One of the interesting membrane materials is the microbial cellulose membrane, which structure is composed of cellulose fibers obtained during biosynthesis by *Acetobacter* bacteria [1]. This membrane is used in form of thin sheets as a membrane dressing to heal burns [2], venous tibia ulceration [3, 4] and in production of prosthesis of blood vessels [5]. As opposed to plant cellulose, microbial cellulose has structure composed of thin microfibrils and is hypoallergenic, nontoxic, nonpyrogenic, biodegradable, highly hydrophilic and biocompatible [6]. The studies carried over by means of Mach-Zehnder interferometer show [7], that microbial cellulose membrane undergo phenomena of strong concentration polarization, caused by concentration boundary layers (CBLs), created on both sides of this membrane. The interferograms characterize this phenomena by strong curving of interferometric fringes at the membrane surfaces in the conditions of hydrodynamic stability of CBLs [7,8], while in conditions of hydrodynamic instability these curving of fringes undergo a spatial-temporal destruction. On the basis of interferograms the thicknesses of created CBLs and the moment of transition from non-convective to convective state could be determined [9]. Besides, CBLs created at the surfaces of the membrane are the cause of reduction of volume and solute flows, electric potentials and currents on the membrane [10]. The reduction of these fluxes as a result of concentration polarization of the membrane is the cause of substantial decreasing of the membrane transport parameters.

In laboratory conditions, CBLs can be almost entirely eliminated by intensive mechanical stirring of solutions. Turning off mechanical stirring causes that at membrane surfaces CBLs are created. CBLs act as pseudomembranes connected in series with a real membrane [11, 12] and cause increase of hydraulic and solute transport resistance. CBLs near membrane should be taken into consideration in order to properly describe non-homogeneous solution transport through the membrane by modified Kedem-Katchalsky equations. One of the modification [13], rely on introduction into classic Kedem-Katchalsky equations the coefficient of solute permeability of the CBL/membrane/CBL (CBL/M/CBL) complex (ω_{sc}).

This coefficient depends on solute concentrations and configuration of the membrane system [13, 14]. The experimental results show [14] that values of coefficient ω_{sc} are depended on gravitational stability of density gradients, arisen near membrane surfaces during solute and volume flows through the membrane. Great enough density gradients near membrane surfaces could be the cause of Rayleigh-Benard instability [9, 15].

In this article, the results of experimental studies of time changes of mean NaCl fluxes after turning off mechanical stirring of solutions were presented. NaCl solutions were divided by flat and symmetrical microbial cellulose membrane, oriented in horizontal plane. The changes of solution concentrations in the membrane system, needed for counting of mean NaCl flux through the membrane were determined on the basis of conductivity changes of that solutions, for different initial quotients of concentrations on the membrane. On the basis of these measurements the concentration characteristic of coefficient of concentration polarization (relative coefficient of permeability of CBL/M/CBL complex) was elaborated for steady states. Two configurations of the membrane system were taken into consideration: configuration with higher density solution under the membrane (A) and over the membrane (B). Interpretation of experimental results was performed using spatial-temporal model of evolution of CBLs, based on the Kedem-Katchalsky equations for membrane.

THEORY

Most studies of electrolyte transport through biological and artificial membranes are interpreted in terms of the Kedem-Katchalsky model equations (KK-model) derived from irreversible thermodynamics [11]. For homogeneous and dilute binary electrolyte solutions (for example single-salt system), these Equations are

$$J_v = L_p(\Delta P - \sigma_s \Delta \pi_s) + \beta I \quad (1)$$

$$J_s = (1 - \sigma_s) \bar{C}_s J_v + \omega_s \Delta \pi_s + \frac{\tau_s}{zF} I \quad (2)$$

where J_v and J_s are the volume and solute fluxes, I is the electrical current density, $\Delta P = P_h - P_l$ is the hydrostatic pressure difference, $\Delta \pi_s = RT(C_h - C_l)$ is the osmotic pressure difference, $\bar{C}_s = (C_h - C_l)[\ln(C_h C_l^{-1})]^{-1}$ is an average solute concentration, C_h and C_l ($C_h > C_l$) are the solution concentrations, L_p is the hydraulic permeability coefficient of the membrane, σ_s is the solute reflection coefficient, β is the electroosmotic permeability

coefficient, ω_s is the solute permeability coefficient and τ_s is the transport number. The definition of transport coefficients L_p , σ_s , β , ω_s and τ_s are presented in ref. [11]. These coefficients are each commonly measured in a separate experiment in conditions of homogeneity of solutions separated by membrane.

When $I=0$, the Eqs. (1) and (2) looks like for non-electrolyte solutions [11], so in order to characterize transport properties of the membrane it is sufficient to determine parameters L_p , σ_s and ω_s for homogeneous solutions. For non-homogeneous solutions (without mechanical stirring), when the CBLs build up near membrane, the decrease of osmotic pressure on the membrane to value $\Delta\pi_s = RT(C_i - C_e)$ is observed. This means that solute concentration on the borders membrane/solutions: in the chamber with higher concentration (C_h) decreases to C_i , while in the chamber with lower concentration (C_l) increases to C_e . Mechanical stirring of solutions causes diminishing of CBLs thicknesses, depended on intensity of mechanical stirring of solutions [13, 14, 16]. Turning off mechanical stirring lead to increase of CBLs thicknesses in time as a result of diffusion [14, 17]. Taking it into consideration, it can be assumed that in the case without mechanical stirring solutions with concentrations C_h and C_l are divided by complex CBL/M/CBL, which transport properties are determined by coefficients: L_{pc} , σ_{sc} and ω_{sc} . In the previous papers [13, 14] it was shown that for osmotic membranes $L_p = L_{pc}$. Next, parameters σ_s and ω_s can be transformed to parameters $\sigma_{sc} = \zeta_{sO}\sigma_s$ and $\omega_{sc} = \zeta_{sD}\omega_s$ by coefficients of concentration polarization ζ_{sO} and ζ_{sD} , which fulfill conditions $0 \leq \zeta_{sO} \leq 1$ and $0 \leq \zeta_{sD} \leq 1$ (for osmotic membranes $\zeta_{sO} = \zeta_{sD}$).

In order to determine the coefficient ζ_{sD} the following considerations will be carried out. In the case of membrane system with mechanical stirring of solutions the coefficient of solute permeability is determined by expression

$$\omega_s = \left(\frac{J_s}{RT(C_h - C_l)} \right)_{J_v=0, I=0} \quad (3)$$

where J_s , J_v and I are suitably solute, volume fluxes and density of electrical current through the membrane during mechanical stirring of solutions, RT is the product of gas constant and thermodynamic temperature. Turning off mechanical stirring causes decrease of solute flux to J_{sc} , dependent on configuration of the membrane system. In connection with this coefficient of solute permeability for complex CBL/M/CBL is determined by Equation

$$\omega_{sc} = \left(\frac{J_{sc}}{RT(C_h - C_l)} \right)_{J_{vc}=0, I_c=0} \quad (4)$$

where J_{sc} , J_{vc} and I_c are suitably solute, volume fluxes and density of electrical current through complex CBL/M/CBL.

Dividing sides of Equations (4) and (3) we get

$$\zeta_{sD} = \frac{\omega_{sc}}{\omega_s} = \frac{(J_{sc})_{J_{vc}=0, I_c=0}}{(J_s)_{J_{vc}=0, I_c=0}} \quad (5)$$

where

$$(J_s)_{J_{vc}=0, I_c=0} = \left(\frac{1}{S} \frac{dn_s}{dt} \right)_{J_{vc}=0, I_c=0} \quad (6)$$

$$(J_{sc})_{J_{vc}=0, I_c=0} = \left(\frac{1}{S} \frac{dn_{sc}}{dt} \right)_{J_{vc}=0, I_c=0} \quad (7)$$

and S is the membrane surface, dn_s and dn_{sc} are quantity of moles of solute permeating suitably through the membrane during mechanical stirring of solutions (in conditions of homogeneity of solutions) and through complex CBL/M/CBL (in conditions of non-homogeneity of solutions) during time dt . One should be to state that Equations (1) and (2) likewise Eqs. (6) and (7) represent temporary fluxes through the membrane. It means that change of conditions on the membrane influence the values of these fluxes. Regarding this, measurement of solute fluxes through the membrane during time Δt , is the measurement of the mean values of fluxes in that time, especially in the case of non-homogeneity conditions.

Using Equation (1) with assumption $J_{vc}=0$ and $I=0$, the mean solute flux through the complex CBL/M/CBL (\bar{J}_{sc}) and through the membrane (\bar{J}_{sm}) during time $\Delta t=t_1$ can be written in the form

$$\bar{J}_{sc} = \frac{\omega_{sc}RT}{t_1} \int_0^{t_1} (C_h - C_l) dt = \omega_{sc}RT(C_h - C_l) \quad (8)$$

$$\bar{J}_{sm} = \frac{\omega_sRT}{t_1} \int_0^{t_1} (C_i - C_e) dt \quad (9)$$

As results from Equation (9) in order to count changes in time of NaCl flux through the membrane after turning off mechanical stirring of solutions, the changes in time of solute concentrations at membrane surfaces are needed. In the case of zero value of volume flux

through the membrane ($J_v = 0$) in the steady state with assumption of this same fluxes $J_{sm} = J_{sc} = J_{sl} = J_{sh}$ in CBL/M/CBL complex the Equation [11]

$$\frac{1}{\omega_{sc}} = \frac{1}{\omega_s} + \frac{RT(\delta_l + \delta_h)}{D_s} \quad (10)$$

is fulfilled. $J_{sl} \cong -D_s \frac{C_e - C_l}{\delta_l}$ and $J_{sh} \cong -D_s \frac{C_h - C_i}{\delta_h}$ are fluxes through CBL suitably in the chamber with lower and greater NaCl concentrations, D_s is the mean diffusion coefficient of solute and δ_l and δ_h are thicknesses of CBLs in the membrane system, formed suitably in chambers with lower (C_l) and higher (C_h) concentrations. Using assumptions for steady state $J_{sm} = J_{sc} = J_{sl} = J_{sh}$ and Equations (1), (2) and (10), with assumptions $I=0$ and $J_v=0$, established during measurements, we get equation determining difference of NaCl concentrations at membrane surfaces in the form [18]

$$C_i - C_e = \left[1 - \frac{RT\omega_s(\delta_l + \delta_h)}{D_s + RT\omega_s(\delta_l + \delta_h)} \right] (C_h - C_l) \quad (11)$$

Using Equation (5) with assumption for steady state $J_{sm}=J_{sc}$ what means that $\omega_s RT(C_i - C_e) = \omega_{sc} RT(C_h - C_l)$, the coefficient of concentration polarization of the membrane can be written as

$$\zeta_{sD} = \frac{C_i - C_e}{C_h - C_l} \quad (12)$$

Taking into consideration Equation (11) in Equation (12) we get

$$\zeta_{sD} = \frac{D_s}{D_s + RT\omega_s(\delta_l + \delta_h)} \quad (13)$$

In Equation (11) the difference of concentrations at membrane surfaces is the function of CBLs thicknesses. When $J_v = 0$ the difference between CBLs thicknesses in chambers is small, so in order to simplify the model of concentrations changes, CBLs thicknesses were assumed to be equal. Time evolution of CBLs thicknesses depends on configuration of the membrane system. As results from [7, 19] thickness of CBL for stable configuration (with lower density solution over the membrane) as a function of time can be presented in the form

$$\delta_A(t) = a\sqrt{\pi D_s t} \quad (14)$$

where: a is the fitting coefficient of model data to experimental results and D_s is the diffusion coefficient of NaCl in solution. From Equation (14) it results that CBL thickness δ_A grows in time dependently on solute diffusion coefficient. For unstable configuration (with solution of

higher density over the membrane), after growing of CBL thickness in time t_o like for stable configuration (as a result of solute diffusion), the hydrodynamic instabilities appear and cause that CBLs thicknesses oscillate (fluctuate) around mean value $a\sqrt{\pi D_s t_o}$. In this case the changes of thicknesses of CBLs in time after turning off mechanical stirring for unstable (B) configuration will be accepted in the simpler form

$$\delta_B(t) = \begin{cases} a\sqrt{\pi D_s t} & \text{for } t \leq t_o \\ a\sqrt{\pi D_s t_o} & \text{for } t > t_o \end{cases} \quad (15)$$

where t_o is time after which hydrodynamic instabilities appear. As an initial condition the homogeneous solutions in chambers was assumed. The aim of numerical calculations on the basis of equations, resulted from KK model for membrane and CBLs adjacent to the membrane, is determination of changes in time of NaCl flux through the membrane in conditions of non-homogeneity of solutions and its fitting to experimental data.

EXPERIMENTS

Measuring set

The measurements were carried out by means of typical membrane system [20], consisted of two chambers with volume $V=250 \text{ cm}^3$ each, divided by microbial cellulose membrane (*Biofill*, Fibrocel Productos Biotecnologicos Ltd., Curitiba, Brazil) with surface area $S=6.1 \text{ cm}^2$, oriented in horizontal plane. The membrane set contained system of magnetic stirrers. The calibrated pipette was joined to the chamber with solution of lower concentration, while reservoir of solution was joined to the chamber with solution of higher concentration. The aqueous NaCl solutions were used. Lower concentration at the initial moment amounted to $C_l = 0.01 \text{ mol m}^{-3}$, while higher concentration (C_h) in the second chamber has been changed in the range from 5 to 100 mol m^{-3} . The membrane system was thermostated and temperature of solutions amounts to $T=295\pm0.5 \text{ K}$. The measurements were carried out for both configurations of the membrane system. In configuration A solution with lower NaCl concentration (lower density) was over the membrane, while in configuration B solution with lower NaCl concentration was under the membrane. At the initial moment the solutions in chambers were homogeneous, it was assured by mechanical stirring of solutions.

The procedure of determination of fluxes \bar{J}_s , \bar{J}_{sc} and coefficients

ω_s, ω_{sc}

Using Equations (6) and (7) the mean solute fluxes \bar{J}_s and \bar{J}_{sc} in time Δt can be written as

$$\bar{J}_s = \frac{1}{S} \frac{V(C_l^* - C_l)}{\Delta t} \quad (16)$$

$$\bar{J}_{sc} = \frac{1}{S} \frac{V(C_{lc}^* - C_l)}{\Delta t} \quad (17)$$

where: V is the volume of chamber, C_l is the lower NaCl concentration at the initial moment, C_l^* and C_{lc}^* are NaCl concentrations in chamber with lower NaCl concentration after time Δt , suitably in conditions of homogeneous and non-homogeneous of solutions. The relative changes of solute concentrations caused by its transport through the membrane are greater in the chamber with lower concentration, so the error of measurements of concentration changes in chamber with lower concentration is lower than in chamber with higher concentration.

Taking into consideration Equations (17), (2) and omitting small components with current density and volume flux in Equation (2) (fulfilled for $\Delta P=0$, so the mean solute flux without mechanical stirring of solutions can be written as $\bar{J}_{sc} = \omega_{sc} RT(\bar{C}_{hc} - \bar{C}_{lc})$), the coefficient ω_{sc} can be written in the form

$$\omega_{sc} = \frac{V (C_{lc}^* - C_l)}{SRT(\bar{C}_{hc} - \bar{C}_{lc})\Delta t} \quad (18)$$

where $\bar{C}_{hc} = \frac{1}{2}(C_{lc}^* + C_h)$ and $\bar{C}_{lc} = \frac{1}{2}(C_{lc}^* + C_l)$ are mean concentrations in chambers with solutions suitably with higher and lower concentration in conditions without mechanical stirring of solutions in time Δt .

Determination of permeability coefficient for membrane (ω_s) requires to exclude CBLs during measurement, using intensive mechanical stirring of solutions. In this case the homogeneity of solutions can be assumed, what means that $C_i \approx C_h$ and $C_e \approx C_l$. Taking into consideration mean solute flux through the membrane in the form (16) and Equation (2) with assumptions of omitting of small components with current density and volume flux (fulfilled for $\Delta P=0$, so the mean solute flux during mechanical stirring of solutions can be written as $\bar{J}_s = \omega_s RT(\bar{C}_h - \bar{C}_l)$), the coefficient ω_s can be written in the form

$$\omega_s = \frac{V(C_l^* - C_l)}{SRT(\bar{C}_h - \bar{C}_l)\Delta t} \quad (19)$$

where $\bar{C}_h = \frac{1}{2}(C_h^* + C_h)$ and $\bar{C}_l = \frac{1}{2}(C_l^* + C_l)$ are the mean concentrations in chambers with solutions suitably with higher and lower concentrations during mechanical stirring of solutions in time Δt . Acceptance of mean concentrations during solute transport through the membrane in Equations (18) and (19), allow to take into consideration changes of concentrations in chambers during measurements. Dividing sides of Equations (18) and (19) we get

$$\zeta_s = \frac{[(C_h^* - C_l^*) + (C_h - C_l)](C_{lc}^* - C_l)}{[(C_{hc}^* - C_{lc}^*) + (C_h - C_l)](C_l^* - C_l)} \quad (20)$$

In order to determine the NaCl permeability coefficient for membrane (ω_s), the chambers of the membrane system were filled in with solutions, one of them with higher concentration $C_h = 10 \text{ mol m}^{-3}$, and the second with lower concentration $C_l = 0.01 \text{ mol m}^{-3}$. Next, the solutions were stirred during 30 minutes with rate 500 rpm, in conditions $J_v = 0$ and $I = 0$. The conductivity of solutions before filling in and after 30 minutes of solute transport through the membrane during mechanical stirring of solutions were measured. After that, using the experimentally determined dependence of conductivity of NaCl solutions as a function of concentration, the concentrations of solutions were determined. Next, the coefficient of NaCl permeability (ω_s) for membrane *Biofill* was determined on the basis of Equation (19). This procedure was repeated for this same lower concentration ($C_l = 0.01 \text{ mol m}^{-3}$) and for higher concentrations $C_h = 50$ or 100 mol m^{-3} , six time for each C_h . The experimentally determined dependence of NaCl conductivity as a function of concentration is shown in Figure 1 (in logarithmic scales). This dependence can also be presented in the form

$$\kappa = \frac{\partial \kappa}{\partial C} \times C + \kappa_o \text{ where } \frac{\partial \kappa}{\partial C} = 1.22 \times 10^4 \mu\text{S m}^2 \text{ mol}^{-1} \text{ and } \kappa_o = 1.5 \times 10^2 \mu\text{S m}^{-1}.$$

In the case of measurement of mean NaCl fluxes through the membrane in A or B configuration in time $\Delta t = t_1$, after filling in of chambers with solutions suitably with C_h and C_l concentrations, the solutions were not mechanically stirred. Next, after time $\Delta t = t_1$, the solutions were poured out, conductivity of solutions were measured and using the dependence of NaCl solution conductivity on NaCl concentration (Fig. 1), the concentrations of solutions were determined. After that, using Equation (18) the mean flux J_{sc} through the complex CBL/M/CBL in time $\Delta t = t_1$ was counted. These procedure of mean flux J_{sc} measurements for

time t_1 equal to 5, 10, 30, 60 and 120 minutes were repeated. The maximal error of mean flux J_{sc} measurement was lower than 8%.

RESULTS AND DISCUSSION

The coefficient of NaCl permeability for the membrane *Biofill*, determined accordingly to the method described in experimental part of this article, amounts to $\omega_{sB} = (17.1 \pm 0.6) \times 10^{-10} \text{ mol N}^{-1} \text{ s}^{-1}$ and is higher than coefficient of NaCl permeability for acetate cellulose membrane, which amounts to $\omega_{sN} = 14.3 \times 10^{-10} \text{ mol N}^{-1} \text{ s}^{-1}$ [21]. This means that small ions better permeate through the microbial cellulose membrane than through acetate cellulose membrane, and taking into consideration great hydraulic permeability coefficient of microbial cellulose membrane $L_p = 6.6 \times 10^{-11} \text{ m}^3 \text{ N}^{-1} \text{ s}^{-1}$ and its small reflection coefficient $\sigma = 0.0036$ [18] we can also state that selectivity of microbial cellulose membrane is very small.

In order to determine influence of CBLs build up on NaCl transport through the membrane *Biofill* in horizontal plane and for configuration A and B, the mean NaCl fluxes through this membrane were measured in conditions without mechanical stirring of solutions. The dependencies of time characteristics of mean NaCl fluxes through the membrane *Biofill* for configuration A (graph A) and for configuration B (graph B) are presented in Figure 2. The concentrations in chambers at the initial moment were: $C_l = 0.01 \text{ mol m}^{-3}$ while C_h equals to 5, 10, 50 or 100 mol m^{-3} . The mean fluxes J_{sc} were experimentally determined on the basis of Equation (17) (points in Figure 2) and counted from Equation (9) (solid lines in Figure 2). The calculations were performed by means of computer program MathCad2000. Fitting of data from the model to experimental results required assumption of coefficients of the model in Equations (14) and (15) as: $D_s = 1.47 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, $\alpha = 0.67$ and times after which the hydrodynamic instability in the membrane system for configuration B appeared: $t_o = 4.5 \text{ min}$ for $C_h = 5 \text{ mol m}^{-3}$; $t_o = 3.0 \text{ min}$ for $C_h = 10 \text{ mol m}^{-3}$; $t_o = 1.0 \text{ min}$ for $C_h = 50 \text{ mol m}^{-3}$; $t_o = 0.8 \text{ min}$ for $C_h = 100 \text{ mol m}^{-3}$.

The way of changes in time of NaCl fluxes, shown in Figure 2 are similar for different initial C_h concentrations. The main differences between fluxes results from different values of concentration gradients on the membrane at the initial moment. The greatest flux changes are observed at the first few minutes after filling in the chambers by solutions and is connected with CBLs build up at the membrane surfaces. From Figure 2 it results that changes of mean

NaCl fluxes in time are smaller and smaller, because the CBLs build up in time is slower and gradients of concentrations on the membrane are lesser. It can be assumed, that after 60 minutes the stable states for membrane system were established. Besides, for studied range of concentrations time characteristics of mean NaCl fluxes through the membrane depends on configuration of the membrane system. For the NaCl concentrations lower than 10 mol m^{-3} at first ten minutes after filling in of chambers with solutions the NaCl fluxes for both configurations do not differ from each other. The reason of that is the CBLs build up only by diffusion. After that time the NaCl fluxes for configuration A are lower than for configuration B. In configuration A, gradients of solute concentration (solution density) are directed as the gravitational vector, so it causes that only the diffusion is the reason of CBLs thicknesses increase. In configuration B, as a result of solute diffusion in CBLs the layers with higher density arise over the layers with lower density. In that case, suitably high gradient of concentration (density) in CBLs, directed in opposite direction to gravitational vector, can be the cause of hydrodynamic instabilities in near membrane areas.

Hydrodynamic instabilities relay on relocating of liquid fragments, causing in effect equalization of concentrations in CBLs in each of chambers and decrease of CBLs thicknesses. These perturbations cause also concentration changes at membrane surfaces and as a reason of that NaCl flux in configuration A is lower than in B. Besides, as results from Figure 2 it can be stated that mean NaCl fluxes in configuration B earlier attain stable states than in configuration A. For concentrations greater than 10 mol m^{-3} the difference between configurations A and B appears in time lower than 2 minutes. At the initial moment, the greater NaCl fluxes are observed for greater concentration differences between chambers and this is the reason that after shorter time than for lower solute concentrations, sufficient gradient of solute concentration (solution density) appears near membrane in B configuration and causes hydrodynamic instabilities.

Analyzing changes of mean NaCl fluxes through the membrane it can be stated that in the membrane system the complex CBL/M/CBL arises and depends on configuration of the membrane system. The permeability of that complex in steady states can be determined by coefficients α_c or ζ_{sD} , counted on the basis of Equations (4) or (13) and (20). The dependencies of coefficient ζ_{sD} in steady states on mean solute concentration in the membrane at the initial moment ($\bar{C}_s = (C_h - C_l)[\ln(C_h C_l^{-1})]^{-1}$) for configuration A (graph A) and B (graph B) are presented in Figure 3. Solid lines were counted on the basis of Equation (13), while points from Equation (21).

From Figure 3 it results that the concentration polarization coefficient ζ_{sD} for configuration B is more than three times greater than for configuration A in the whole range of studied NaCl concentrations. The reason of that is that in configuration A, which is the stable configuration, the CBLs thicknesses are greater than in configuration B. Hydrodynamic instabilities appearing in configuration B cause smaller CBLs influence on NaCl membrane transport by destructing of CBLs. This is the cause of greater NaCl fluxes and coefficients ζ_{sD} and ω_{sD} in comparison to fluxes and suitable coefficients in configuration A. Besides, for configuration A the coefficient ζ_{sD} do not depends on mean NaCl concentration in membrane, while for configuration B ζ_{sD} increases with increase of \bar{C}_s . Greater values of ζ_{sD} for greater mean NaCl concentrations in membrane *Biofill* indicate on greater intensity of hydrodynamic instabilities in near membrane area, and more effective destruction of CBL/M/CBL complex.

CONCLUSIONS

1. Using the method of determining of solution concentrations in chambers by measurement of conductivity of that electrolyte solutions, the coefficient of permeability of microbial cellulose membrane *Biofill* for NaCl solutions was determined and amounts to: $\omega_B = (17.1 \pm 0.6) \times 10^{-10} \text{ mol N}^{-1} \text{ s}^{-1}$.
2. Time changes of mean solute flux through the membrane are the reflection of CBLs changes near membrane surfaces. It was found that solute fluxes through the membrane oriented in horizontal plane depend on configuration of the membrane system. In the case of configuration A, CBLs build up proceeds only by diffusion and the solute fluxes are lower than fluxes observed in these same conditions in configuration B, for which except diffusion hydrodynamic instabilities appear, causing decrease of CBLs thicknesses. Time after which the difference between fluxes in configurations A and B are observed is shorter for greater quotient of concentrations in chambers at the initial moment.
3. In the case of stable configuration (A) the coefficient of concentration polarization for the membrane *Biofill* (ζ_{sD}) does not depend on initial mean concentration in the membrane and is over three times lower than ζ_{sD} for configuration B. Increase of mean concentration in the membrane for configuration B causes increase of concentration polarization coefficient value, caused by more intensive hydrodynamic

instabilities in that configuration of the membrane system for large enough concentration (density) gradients in CBLs.

4. The fitting of results from the model to experimental data is better for longer times of measurement of NaCl fluxes through the membrane. It results from the fact that the KK model describe steady states of the membrane system.

LITERATURE

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Adress for correspondence

Department of Biophysics

Chair of Biomedical Fundamentals of Sport

Częstochowa University of Technology

PL-42200 Częstochowa, 36b Armia Krajowa Al. Poland

tel. (034) 325 0395, tel./fax (034)361 3876

e-mail: ajslezak@zim.pcz.pl

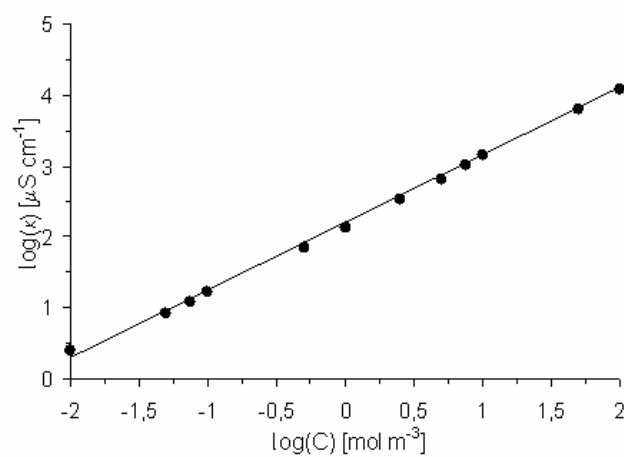


Fig. 1. Conductivity (κ) of NaCl solution as a function of NaCl concentration (C)

Ryc. 1. Przewodnictwo (κ) roztworów NaCl w funkcji stężenia (C)

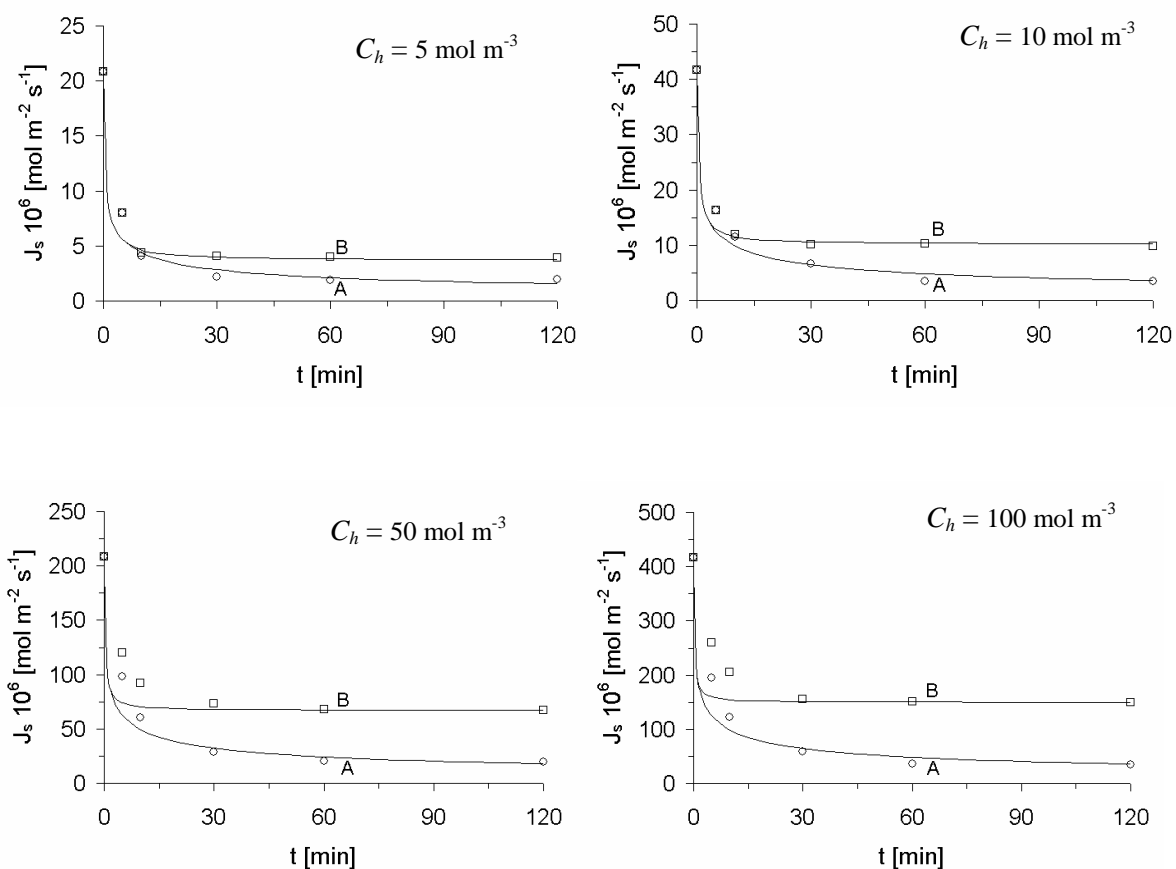


Fig. 2. The mean NaCl flux through the *Biofill* membrane as a function of time for configuration A (graph A) and B (graph B), for concentrations: $C_l = 0.01 \text{ mol m}^{-3}$ and C_h : 5 mol m^{-3} , 10 mol m^{-3} , 50 mol m^{-3} and 100 mol m^{-3}

Ryc. 2. Średni strumień NaCl przez membranę *Biofill* w funkcji czasu dla konfiguracji A (wykres A) i B (wykres B), dla stężeń $C_l = 0.01 \text{ mol m}^{-3}$ i C_h : 5 mol m^{-3} , 10 mol m^{-3} , 50 mol m^{-3} and 100 mol m^{-3}

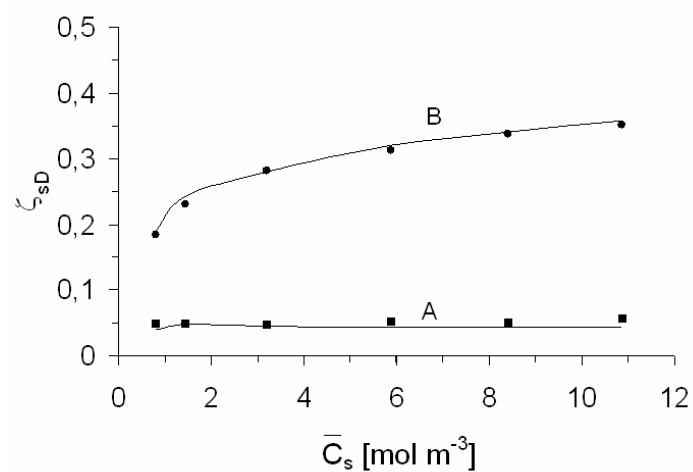


Fig. 3. The coefficient of concentration polarization (ζ_{sD}) in steady states as a function of mean NaCl concentration in the membrane for configuration A (graph A) and B (graph B).

Ryc. 3. Współczynnik polaryzacji stężeniowej (ζ_{sD}) w stanie ustalonym, w funkcji średniego stężenia NaCl w membranie dla konfiguracji A (wykres A) i B (wykres B).